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*Published in:*  
Applied Physics Letters

*DOI:*  
[10.1063/1.2360910](https://doi.org/10.1063/1.2360910)

*Publication date:*  
2006

*Citation for published version (APA):*

Evans, D. A., Vearey-Roberts, A. R., & Poolton, N. R. (2006). Locating hexagonal and cubic phases in boron nitride using wavelength-selective optically detected x-ray absorption spectroscopy. *Applied Physics Letters*, 89(16). <https://doi.org/10.1063/1.2360910>

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# **Locating hexagonal and cubic phases in boron nitride using wavelength-selective optically-detected x-ray absorption spectroscopy**

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## **Abstract**

Cubic and hexagonal phases of boron nitride (cBN, hBN) have been identified and located using optically-detected x-ray absorption spectroscopy (ODXAS). Each phase was identified by distinct resonance features in the B K-edge absorption spectra. In a mixed-phase sample of predominantly cBN, combined ODXAS and electron yield measurements suggested near-surface localisation of hBN. Using x-ray excited luminescence, emission bands due to each phase were identified and applied in wavelength-selective ODXAS to locate surface and bulk hBN phases. These combined techniques provide a method of correlating the local structure and optical emission in these wide-gap semiconductors.

Cubic boron nitride (cBN) shares many desirable properties with diamond; for example it has comparable hardness and thermal conductivity and has a similar, but larger, electronic band gap <sup>1,2</sup>. It surpasses diamond in some applications, such as cutting tools for ferrous materials, and offers a wider parameter space for addressing issues such as doping and contact formation in electronic and optoelectronic devices. As crystal quality continues to improve, it is essential to evaluate the full optoelectronic potential of these wide-gap materials, in particular through correlating physical and electronic structure with light absorption and emission. Although high quality crystals of cBN have been grown by high temperature, high pressure (HPHT) synthesis <sup>3</sup> and chemical vapour deposition (CVD) <sup>4,5</sup> and some device structures have been demonstrated <sup>6</sup>, progress has been less rapid than in synthetic diamond growth, where functional devices have already been demonstrated <sup>7</sup>. An important difference between cBN and diamond is that the more stable hexagonal phases are electronically very different. Hexagonal BN (hBN) is structurally similar to graphite, but it is a wide-gap semiconductor with a similar band gap to cBN <sup>1</sup>. It is a very efficient emitter of visible light due to its quasi-direct band gap as opposed to the indirect gap of cBN and diamond <sup>2,8</sup>. BN also exhibits other crystal structures (e.g. wurzite, rhombohedral) <sup>9-11</sup>, but the two main structures are cBN and hBN and this study is focused on these two materials, using x-ray absorption combined with light emission to locally distinguish the two phases. Very few techniques are able to simultaneously provide parallel information on physical and electronic structure and even fewer on structure and light absorption/emission. Two synchrotron radiation techniques (x-ray excited optical luminescence (XEOL) and optically-detected x-ray absorption spectroscopy (ODXAS) applied in parallel provide such a combination <sup>12,13</sup>. In ODXAS, structural information in wide-gap materials such as boron nitride is obtained from measurements of luminescence yield as the incident x-ray energy is scanned across the B and N K-edges. This method is analogous to electron yield techniques (Near-Edge X-ray

Absorption Fine Structure (NEXAFS) or X-ray Absorption Near-Edge Spectroscopy (XANES)) that have already been widely applied to boron nitride to identify cubic and hexagonal phases<sup>9-11</sup>. Strong B1s- $\pi^*$  and N1s- $\pi^*$  resonances are observed only for sp<sup>2</sup>-bonded materials and the corresponding 1s- $\sigma^*$  resonance features are different for the various polytypes<sup>10</sup>. However, locating the components in mixed-phase samples is limited with electron yield techniques as they are usually area-integrating and probe only the near-surface region. Optical detection can remove these limitations and can be applied at the same time to probe both the surface and bulk bonding. Coupled with XEOL, local structure can be correlated with luminescence from impurity and defect levels within the energy band gap, providing information that would previously have required separate XANES and photoluminescence experiments. For BN, soft x-ray excitation is particularly useful for detecting band-edge UV luminescence that is not always accessible using laser excitation.

XANES spectra taken in total electron yield (TEY) mode and the corresponding ODXAS spectra taken in total luminescence yield (TLY) mode for three BN samples are shown in Figure 1. The data were recorded at beamline MPW6.1 at the UK synchrotron radiation source (SRS) at the Daresbury laboratory. All samples were cooled to 10K in vacuum. Emitted light was collected by a broad-band photomultiplier tube for TLY ODXAS and a grating monochromator was used for XEOL and for partial luminescence yield (PLY) ODXAS. BN1 is a pure hBN powder showing a single Raman phonon line at 1367 cm<sup>-1</sup>, BN2 is a mixed-phase (cBN/hBN) sample (Element Six Ltd) that has dominant cBN Raman phonon lines at 1054 cm<sup>-1</sup> (TO) and 1304 cm<sup>-1</sup> (LO) with no hBN lines and BN3 is a single-phase cBN sample (Element Six Ltd), consisting of uniform single crystals of dimension ~20  $\mu$ m and that exhibit well-defined Raman phonon lines at 1055 and 1305 cm<sup>-1</sup>. The morphology and size distribution of the cBN crystals were confirmed using Field-emission Scanning Electron

Microscopy. The two single-phase materials can be readily distinguished by the distinct B1s- $\pi^*$  resonance peak at a photon energy of 191.8 eV that is present in BN1 (and BN2) but absent in BN3 (Figure 1). The near-edge structure between 197 and 200 eV for BN1 is due to B1s- $\sigma^*$  resonances. These are significantly different from the corresponding B1s- $\sigma^*$  resonance features in samples BN2 and BN3. BN2 contains features of both hBN and cBN, even though there is no bulk hBN Raman peak. This suggests that the hBN component is not long-range. The TLV spectra (dashed lines) in Figure 1 are inverted with respect to the TEY spectra (solid lines). The decrease in luminescence intensity with increasing x-ray absorption is consistent with emission from bulk materials, and so the grains in BN1 must be significantly larger than the electron mean free path. BN2 and BN3 are known to consist of crystals of dimension  $\sim 1$  and  $\sim 20$   $\mu\text{m}$ . The essential features for all samples are reproduced in both TEY and TLV, but, for BN2, the B1s- $\pi^*$  resonance peaks are more prominent in the TEY spectra. Since the ODXAS technique is more bulk-sensitive than XANES (the probing depths are  $\sim 200$  and  $\sim 1$  nm respectively), the data of Figure 1 suggest that the hBN phase in BN2 is located near the surface.

The hBN phase in BN2 can be more definitively located by applying wavelength-selectivity to the collection of the emitted luminescence. All three materials were strongly luminescent in the visible and UV region under soft x-ray irradiation and the XEOL spectra for the three BN samples, recorded with an x-ray excitation energy of 300 eV are shown in Figure 2. The raw data (black curves) are plotted along with fitted components and their sum (grey curves). The inhomogeneously-broadened bands are best represented by Gaussian functions and the sharp peaks superimposed on the broad bands are related to electron-phonon coupling in these ordered materials<sup>14</sup>. The dominant bands are around 3 - 4 eV in all cases and, although the main bands appear similar, there are distinct differences in the energy and

width of these bands for BN1 (hBN) compared to BN2 and BN3. The lower intensity 5.5 eV band is observed only for the pure hBN sample (BN1) and the mixed-phase sample (BN2). Emission peaks at 3 and 4 eV have been widely reported for BN in photoluminescence<sup>15,16</sup>, ionoluminescence<sup>17</sup> and cathodoluminescence<sup>18-21</sup> studies and have been ascribed variously to vacancy and impurity (mainly C) states. These soft-x-ray XEOL measurements for this material (Figure 2) compare favorably to those obtained using laser and electron beam excitation. The well-resolved peaks for BN2 and BN3, arising from electron-phonon coupling to discrete photon energies, reflect their crystalline quality and such structure has only been this clearly observed in one, area-selective cathodoluminescence study<sup>18</sup>. The data quality enables the zero-phonon lines (ZPL) to be identified for BN2 (ZPL = 3.56 eV) and BN3 (ZPL = 3.56 eV and ZPL = 4.92 eV). The high-energy luminescence peaks in BN1 and BN2 are also ascribed to phonon-coupled electronic transitions related to the same shallow defect (ZPL = 5.62 eV). This group of peaks appears to be hBN-related as they are completely absent for BN3. Their presence in the XEOL spectrum for BN2 (Figure 2) is consistent with the XANES/ODXAS data that suggest that BN2 is predominantly cBN with some phase-separated hBN. The presence of features associated with phonon-coupled transitions is a further indicator of the long-range order in all materials. Using the main emission bands revealed in XEOL, wavelength-selective ODXAS was then applied to locate the hBN and cBN phases in the mixed-phase material, BN2.

ODXAS data for the three BN samples were recorded in PLY mode by selecting wavelengths corresponding to the maxima of the luminescence features (225 and 350 nm for BN1; 393 , 314 and 226 nm for BN2; 305 nm for BN3). For samples BN1 and BN3, the PLY spectra (not shown) corresponded to the TLY data, as expected for these single-phase materials. However, the mixed-phase sample BN2 showed very different spectra for the three emission bands, as shown in Figure 3. At the longest wavelength (a), the spectrum is

dominated by cBN emission features (see Figure 1 for comparison), indicating that the states responsible for this luminescence are located largely within the cBN crystals. The presence of a small  $\pi^*$  resonance dip suggests some  $sp^2$  bonding within the cBN crystals. At wavelength 314 nm (b), there is an additional  $\pi^*$  resonance peak (positive with respect to the non-resonant background) and a small increasing  $\sigma^*$  edge indicating a contribution from near-surface hBN. At the shortest wavelength (c), corresponding to emission from shallow defect levels, the spectrum is entirely that of hBN and the resonance features are positive with respect to the non-resonant background, indicating an increase in luminescence intensity with increasing x-ray absorption. The hBN material giving rise to the 5.5 eV band-edge luminescence emission of sample BN2 must therefore be located within the topmost ~1nm. Wavelength-selective ODXAS has thus been able to locate the hBN phase in sample BN2 on the surface of the cBN crystals and has shown that all the observed UV emission from this material is due to this superficial hBN layer. No other approach is able to detect and identify the location and light-emitting properties of these two phases in this way. The combined application of x-ray-absorption and light emission using synchrotron radiation excitation provides a valuable tool for the characterisation of this emerging wide-gap optoelectronic material.

## **Acknowledgements**

This work was supported by the UK Research Councils (EPSRC and CCLRC). AVR acknowledges the support of HEFCW in the award of a fellowship. Element Six Ltd. are thanked for the provision of samples, I. ap Gwynn and S. Wade are thanked for FESEM imaging and D. Jones for Raman spectroscopy measurements.

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